PATENT SPECIFICATION

COMPLETE SPECIFICATION.

Process for Smelting Ores to Metal, Matte and Slag.

I, HARALD SKAPPEL, of 5b, Raadhus-gatan, Oslo, Norway, a Subject of the King of Norway, do hereby declare the nature of this invention and in what
5 manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to an improved method of smelting ores, and is applicable
10 both to the ferrous and to the non-ferrous metal industries. While the invention is particularly applicable to the treatment of sulphide ores, it is applicable also to the treatment of oxidic ores as is herein-
15 after explained.

In the existing metallurgical matte-smelting, operations are carried on with slags rich in ferrous oxide (over 15% of FeO) and with mattes having a high
20 power of dissolving pure metal.

This is subject to the disadvantage that large amounts of pure metals thus dissolved were liable to be lost, and in any case, the recovery or isolation of the same
25 from the mattes is troublesome and costly.

The present invention aims at overcoming this difficulty by producing a clean-cut separation of slag, matte and metal or metals in one operation, starting
30 from the ore, the smelting process being thus considerably simplified and cheapened.

To this end the invention contemplates regulating or influencing the usual smelt-
35 ing operations by suitably adjusting the composition of the charge and by means of certain additions hereinafter more fully set forth in such a manner that the melt segregates into three or more molten
40 layers, namely, slag, matte and crude metal or metals, these layers being in chemical equilibrium with one another, and having the following characteristic features:

45 The slag (silicates) obtained in accordance with the present invention contains less than 15% of FeO.

The matte consists chiefly of heavy metal sulphides and in addition thereto a certain amount of light metal sulphides,
50 the function of which latter will hereinafter be more fully explained.

The layer or layers of crude metal or metals, for example crude iron and a separate layer of non-ferrous metals, con-
55 tain the metallurgical " speisses " which are in reality to be considered and treated as crude metals.

It should be noted that the sulphides employed in the present invention are not
60 non-metallic sulphides in the hitherto accepted sense of the words, i.e. they are not compounds of non-metallic elements with sulphur, but are sulphides of metals with non-metallic physical properties,
65 thus for example they are of non-metallic appearance and conduct an electric current electrolytically.

Now in this connection it has been ascertained that the sulphides of the
70 metals exhibit a graduation of physical properties, and in particular, the metallic properties decrease with increasing heat of formation of the sulphides per gram-atom of sulphur. Thus the heavy metal
75 sulphides such as MoS_2, PbS, CoS, Cu_2S and FeS, for example, have a low heat of formation, (i.e. from 20.2 to 24 kilogram calories per gram-atom of sulphur) and well defined metallic properties, and are
80 able to dissolve pure metal when they are in the molten state.

The light metal sulphides, such as for example, Al_2S_3, MgS and CaS have a high heat of formation, (i.e. from about
85 42 to 94.3 kilogram calories per gram-atom of sulphur) are non-metallic in property and are quite insoluble in pure metals and incapable of dissolving them.

In the following Table, the most usual
90 metallic sulphides are arranged in the order of the increasing heat of formation per gram-atom of sulphur.

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Chemical Formula.	Heat of Formation kilogram calories.	Heat of Formation per Gram-atom of S. kilogram calories.	Nature & Properties.
Ag₂S	3.—	3.—	
HgS	10.6	10.6	
As₂S₃	?	?	
Sb₂S₃	34.4	11.5	
MoS₂	?	?	
NiS	19.3	19.3	"metallic"
PbS	20.2	20.2	
Cu₂S	20.3	20.3	
CoS	21.9	21.9	
FeS (crystalline)	24.—	24.—	
FeS (amorphous)	18.8	18.8	
SnS	?	?	
Cr₂S₃	?	?	"semi-metallic"
CdS	34.4	34.4	
Al₂S₃	126.4	42.1	
ZnS	43.—	43.—	
MnS	45.6	45.6	
MgS	79.4	79.4	
Na₂S	89.3	89.3	
CaS	94.3	94.3	"non-metallic"
SrS	99.3	99.3	
BaS	102.9	102.9	
K₂S	103.5	103.5	
Li₂S	105.—	105.—	

(Line numbers in left margin: 5, 10, 15, 20, 25)

However, all the metallic sulphides, whether of light metals or heavy metals, are mutually soluble with few exceptions, and it has been found that the addition of one or more light metal sulphides to one or more heavy metal sulphides modifies the physical properties of the latter, i.e. the mean heat of formation of the mixed sulphide melts per gram-atom of sulphur is increased, the metallic properties are decreased and consequently the solvent power of the sulphides for pure metals is decreased or disappears entirely, according to the amount of light metal sulphides added.

It has been found in this connection that a sulphide with a mean heat of formation exceeding 40 kilogram calories per gram-atom of sulphur is definitely "non-metallic", whilst a sulphide with a mean heat of formation of less than 24 kilogram calories per gram-atom of sulphur is definitely "metallic".

It has already been proposed to add metallic sulphides with a heat of formation exceeding 40 kilogram calories per gram-atom of sulphur to oxidic or roasted sulphide ores for the purpose of converting the oxides into sulphides during the smelting treatment, and to ores already containing certain amounts of sulphur and moreover sulphides of the said type have already been added in small amounts to ores for the purpose of "splitting up" the melt produced on smelting and separating out the individual components.

The present invention also comprises the use of sulphides of the above kind, and consists in the steps of ascertaining the composition of the ore, calculating the amount of matte that will be formed from a given charge, adding to the charge a quantity of a sulphide with a heat of formation of at least 40 kilogram calories per gram-atom of sulphur, (such as zinc, manganese and sodium sulphides, or of an equivalent quantity of substances capable of forming such sulphides), which is sufficient to raise the mean heat of formation of the matte above 25 kilogram calories, and thereupon smelting the ore together with the usual additions.

Hence in the light of the foregoing, it is possible by means of the present invention to apply these novel principles to the smelting of metallic ores for example, to the smelting of sulphidic iron ores, by the addition of a sulphide of non-metallic character (i.e. a sulphide the heat of formation of which exceeds 40 kilogram calories). In some cases, the ore may already contain substances adapted to form such sulphides i.e. gypsum, when it is only necessary to add sufficient carbon to produce calcium sulphide but in all cases the amount of non-metallic sulphide added must be sufficient to increase the heat of formation of the matte per gram atom of sulphur to between 25 and 38 kilogram calories, when the metallic properties of the matte—i.e. its solvent power for the metal, for example metallic iron—dis-

appears and a segregation of the melt into metal, matte and slag takes place in the molten state.

Thus, for example, in the case of certain iron ores of Minnesota, containing 5 to 10% of manganese and a high phosphorus and sulphur content, by smelting down these ores in the usual furnaces and regulating the composition of the charge so that the matte will contain a high percentage of sulphide of non-metallic character (in this case manganese sulphide), the following products are obtained in chemical equilibrium:—

1). A slag containing about 7% of (FeO + FeS), and having a small manganese content, but which takes up the bulk of the phosphorous contents of the ore.

2). A matte containing 50% of MnS and 50% of FeS (the sulphur contents of the charge being regulated by the addition of MnS). This matte by reason of its high content of MnS separates clean from the crude iron metal in the molten state. Even considerably less manganese sulphide in the matte would cause this separation between the matte and crude metal in the molten state, but it is desirable for other practical reasons to produce a matte with a high manganese content; for example, this matte on roasting yields raw material which is eminently adapted to produce excellent ferro-manganese.

3). Crude white pig iron containing very little manganese, a little phosphorus and having a sulphur content of about 0.3%, which can be further desulphurised by known methods.

It should be realised, that the chemical equilibrium, i.e. the distribution of elements in a triple-phase molten system of metal, matte and slag is dependent on the ratio of the amounts of oxygen and sulphur present to the amounts of other elements present. Thus, for example, if sulphur be added to such a system, then the equivalent amount of metal will be transferred from the metallic layer to the sulphidic layer. If oxygen be added, then the equivalent amount of metal will be transferred from the metal layer to the sulphide layer and simultaneously an equivalent amount of another metal will be transferred from the sulphide layer to the oxide or silicate layer (slag).

Conversely, if oxygen be removed from the system, for example, by reduction with carbon, then the equivalent amount of metal will be transferred from the slag to the matte, and will there precipitate out an equivalent amount of another metal, which will be transferred to the metallic layer.

Moreover, this transference of metals from one phase to another takes place in a definite serial order, both in the case of transference from the silicate phase to the sulphide phase and in the case of transference from the sulphide phase to the metal phase; and yet this is subject to the limitation that it is generally a question of chemical equilibrium resulting in the simultaneous transfer of two or more elements in different amounts.

Hence if it is desired to transfer from the slag to the matte metals which are in the neighbourhood of iron in the serial order of transference, we must necessarily also transform the bulk of the iron oxide into sulphide, i.e. operations must be carried out with a slag having a low iron oxide content; Such metals are copper, lead, and silver, and it follows that with an increasing degree of reduction of the slag, the more complete is the transference of valuable components present to the matte and the raw metals—i.e. the loss by slagging diminishes.

There are three well defined degrees of reduction of the slag (or the system) namely:

1). The ferrous oxide stage characterised by a silicate (slag) which has in general a high FeO content (minimum 8% of FeO + FeS).

2). The calcium sulphide stage characterised by a silicate phase with a low iron (and other heavy metal) content and containing CaO and/or MgO and other light metal oxides and a matte containing CaS and/or MgS.

3). The aluminium sulphide stage characterised by a silicate or oxide-phase slag with a low FeO, CaO and MgO content, and a sulphide phase containing a considerable percentage of Al_2S_3.

A molten system of the ferrous oxide stage such as, for example, the ordinary products of the lead-smelting furnace that are collected on the fore-hearth (the slag containing some 40% of FeO) may be transferred to the calcium sulphide stage by adding a suitable quantity of CaS or MgS whereupon the reaction

$$FeSiO_3 + CaS \rightleftharpoons CaSiO_3 + FeS$$

takes place.

Similarly, this calcium sulphide stage may be transferred to the aluminium sulphide stage by the addition of Al_2S_3.

Hence it can be seen that the composition of the separate molten layers of metal, matte and slag obtained in accordance with the present invention may be controlled at will by varying the degree of reduction of the system, i.e. by adding to the charge prior to smelting, a suitable quantity of reducing carbon or the like.

Moreover, having regard to the nature of the speisses as crude metals and to the

conditions under which they are obtained —i.e. by adding additional ferruginous material to the charges, the composition and the quantity of the speiss precipi- tated on separation from sulphide is so regulated that it constitutes a collecting medium for certain elements in suitable concentration, inasmuch as the end in view is to produce with advantage iron speisses which are not miscible with the crude non-ferrous metals occurring at the same time such as, for example, lead, and which take up certain elements, such as, for example, As, Sb, Ni, Co, Mo, Pt.

In the treatment of lead-silver-copper- ores, the present invention, compared with the old smelting method, produces slags poorer in copper and lead, and results in more complete precipitation of lead, sil- ver and arsenic out of the matte and in the production of a favourable qualitative and quantitative controllable speiss, which separates out of the matte in the molten condition.

If the lead-silver-ores, or copper ores or lead-silver-copper ores, contain con- siderable amounts of zinc, the treatment according to the present invention intro- duces the new method of accumulating the zinc contents of the ore as sulphide in the resulting matte (instead of driving it into the slag as done by the old way of smelting) by keeping (if crude metals are simultaneously present at the same time) the smelting temperature below 1250° C. This may be performed in an electric furnace. But if, for instance, a blast furnace is to be used, which has a very high temperature in the smelting zone, the complex zinc ore is better smelted in the unroasted condition in the blast furnace to slag and matte only, the melting point of the latter being lowered by addition of 8% Na_2S (or Na_2SO_4+ coke) to the charge, and is then, in the fore-hearth, when the temperature has dropped below 1250° C., brought together with, for instance, molten iron or speiss, which precipitates the lead contents out of the matte and gives a molten polyphase system according to the present invention.

EXAMPLE No. 1.

A lead sulphide ore was found to have the following composition:

81.6% Pb
0.91% Cu
0.88% Fe
0.10% As
0.05% Ag
13.31% S
3.00% SiO_2

99.85%

The amount of matte (sulphides of metals other than lead which latter is to be deposited in the metallic condition), formed from 1000 kilograms of ore was then calculated which involved calculat- ing the amount of scrap iron to be added to combine with the excess of sulphur to form ferrous sulphide, which enters into the matte.

It was found that 373.3 kilograms of matte will be produced and that 220.3 kilograms of scrap iron will be required for the said purpose.

From the amount of matte produced the average heat of formation of the matte per gram-atom of sulphur can be calcu- lated using Richards' Metallurgical Tables. It is found that the heat of formation of 373.3 kilograms of matte containing 133.3 kilograms of sulphur is 99,917 kilogram calories. Therefore, the heat of formation per gram-atom of sul- phur is 24 kilogram calories.

The amount of sodium sulphide (having a heat of formation of 89.3 kilogram calories per gram-atom of sulphur) re- quired to bring the average heat of for- mation of the matte per gram-atom of sulphur up to 31 (in order to render the lead practically insoluble therein) is then calculated and is found to be 39 kilograms per 1000 kilograms of ore. (This is added in practice in the form of sodium sulphate and powdered coke in equivalent amounts). Hence the compo- sition of the charge with regard to the matte will be

1000 kilograms of ore
250 kilograms scrap iron (to allow for impurities in the iron)
77 kilograms sodium sulphate
26 kilograms powdered coke

Total 1353 kilograms.

The final composition of the charge is now calculated.

The constituents of the charge are lead ore, scrap iron, limestone, coke and sodium sulphate. The percentage of slag-forming constituents in these materials is calculated, any MgO and FeO being calculated as equivalent amounts of lime for convenience, and it is found from this that about 1000 kilo- grams of charge will have to contain:
724.45 kilograms of lead ore
181.11 kilograms of scrap iron
18 kilograms of powdered coke (approx.)
54 kilograms of sodium sulphate (approx.)
42.26 kilograms of limestone.
The resulting products consist of:

575 kilograms of lead (containing about 0.06% Ag).

328 kilograms of matte of the following composition: 78.4% FeS, 2.9% Cu₂S, 7% Pb, 10.6% Na₂S and 0.4% As₂S₃.

63.7 kilograms of slag of the following composition: 3.0% FeO, 26.2% CaO, 57.8% SiO₂, 8.4% MgO and 4.5% Al₂O₃.

EXAMPLE No. 2.

A complex ore was found to have the following composition: 35.4% Pb, 9.4% Cu, 11.7% Zn, 4.9% Fe, 0.9% As, 17.1% S, 16.3% SiO₂, 1.2% Al₂O₃, 1.1% CaO and 1.7% MgO. The amount of matte formed from a given charge was then calculated, and from it the average heat of formation of the matte per gram-atom of sulphur as set forth in Example 1. Similarly the amount of sodium sulphide required to bring the average heat of formation of the matte per gram-atom of sulphur up to at least 40 kilogram calories per gram-atom of sulphur was calculated, and it was found that (calculated as equivalent amounts of sodium sulphate and coke) 10% of Na₂SO₄ and 6% of powdered coke were required. The ore was accordingly comminuted and mixed with 10% of quicklime, 10% Na₂SO₄ and 6% of powdered coke, agglomerated by moistening and drying and was smelted in a shaft furnace, with the further addition of 20% of slag rich in ferrous oxide, in known manner by means of coke in the form of pieces. An acid slag poor in ferrous oxide and having a low content of heavy metal was obtained, together with the following products which could be separated from each other by tapping:

1). Matte of the composition 8.3% Pb, 20% Cu, 23% Zn, 10.7% Fe, 0.49% As, 80 grams per ton of silver, 9.7% (Na₂S + CaS) as well as S.

2). Speiss of the composition Fe 68.3%, As 24.7% Cu 3.2% Pb not determined.

3). Workable lead containing 580 grams per ton of silver and only 0.56% As. It is to be noted that in consequence of the content of light metal sulphide in the matte, in this method of carrying out the smelting, matte and speiss can be separated in a fluid state by tapping off from the fore-hearth.

EXAMPLE No. 3.

A tin slag from a reverberatory furnace smelting operation was found to contain: 39.4% SiO₂, 14.7% Al₂O₃, 26.2% FeO, 7.9% CaO, 0.5% MgO, 1.7% Na₂O, 8.1% SnO, 1.3% WO₃. The amount of matte (containing tin, tungsten and iron sulphides that would be formed from a given quantity of tin slag, is calculated together with the necessary quantity of gypsum, sodium sulphate and carbon needed to form the sulphides in the matte, and to bring the mean heat of formation thereof up to 25 to 38 kilogram calories. The slag was smelted together with a mixture of gypsum, sodium sulphate and carbon in the calculated proportions. In this operation the tin, tungsten and iron contents of the slag were transferred to a matte containing sodium sulphide which was worked up in known manner into tin, tungsten and iron sulphide.

A further very important application of the process consists in working up certain oxidic ores into sulphides and slags with the aid of material which yields CaS or MgS and in particular ores which contain such oxides of heavy metals which lie in the vicinity of iron or after iron in the serial order of transference from oxide to sulphide, such as for example, the chromium and iron content of chrome-iron-stone, the manganese content of impure manganese ore (containing for example sulphur and phosphorus) the iron and a great part of the titanium content of titanium-iron ores and the like. The process may also, so to speak, be carried out in a fractional manner, insofar as at first only certain constituents are transformed into the sulphide phase by the sparing apportioning of the CaS added, and other constituents are thereupon transformed into a new sulphide phase by the addition of CaS, MgS or Al₂S₃.

Naturally, not only heavy metals, but also light metals can be fractionally transformed in this manner from silicate or oxide into sulphide, for example, potassium, sodium and barium. If the process is carried out with these metals in the same manner as described above with reference to heavy metals care must be taken to ensure the simultaneous presence of a sufficiently large heavy metal sulphide base which is capable of taking up the freshly formed light metal sulphide, since the light metal sulphide would otherwise dissolve in the silicate slags, particularly when the slag is basic. FeS is particularly suitable as a solvent for alkali metal sulphides. However in the production of these light metal sulphides a separation of the silicate phase and sulphide phase can be entirely disregarded, since these light metal sulphides are all water soluble and can therefore be subsequently extracted as a solution from solidified and disintegrated melt by lixiviation with water. In this case it is moreover unnecessary to heat the mass to complete fusion, since a moderate heating up to sintering and transformation is sufficient.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is :—

1). In a method of smelting ores, of the type in which sulphides with a heat of formation of at least 40 kilogram calories per gram atom of sulphur (such as zinc, manganese and sodium sulphides, or an equivalent quantity of substances capable of forming such sulphides) are added to the charges, the steps which comprise ascertaining the composition of the ore, calculating the amount of matte that will be formed from a given charge, adding to the charge a quantity of such a sulphide, which is sufficient to raise the mean heat of formation of the matte above 25 kilogram calories, and thereupon smelting the ore together with the usual additions.

2). Method as set forth in claim 1, in which the mean heat of formation per gram atom of sulphur of the matte formed during the smelting is sufficiently great to render it non-metallic in the sense hereinbefore defined and thus to prevent appreciable quantities of heavy metals remaining dissolved therein, the said metals forming a separate layer below the matte.

3). Method as set forth in claims 1 and 2, in which the matte takes up iron from the slag to replace the heavy metals expelled from the matte, to such an extent that the slag contains a maximum of only 15% FeO.

4). Process as set forth in any of the preceding claims, in which the order to produce an iron speiss which is non-miscible with the crude non-ferrous metals, such as lead, but which will take up elements such as for example, As, Sb, Ni, Co, Mo, Pt, iron is added to the charge in suitable quantity and in the form of for example, ferrous oxide slag, together with coke or material containing silicon or phosphorus, the latter additions being adapted to reduce the melting point of the charge and to produce a more clean-cut separation between the non-ferrous metals and the speiss.

5). A process as set forth in any of the preceding claims, in which the temperature is maintained below the neighbourhood of 1250° C. during the smelting operation.

6). A process for smelting ferrous and non-ferrous ores and metallurgical products substantially as hereinbefore described.

Dated this 3rd day of August, 1928.
ALBERT L. MOND,
19, Southampton Buildings,
Chancery Lane, London, W.C. 2,
Agent for the Applicant.